# VALORIZATION OF LIGNIN IN POLYMER AND COMPOSITE SYSTEMS FOR ADVANCED ENGINEERING APPLICATIONS – A Review

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## Abstract

As fossil fuel resources dwindle and new regulations for a cleaner and safer environment come on stream, there is growing interest in developing new sustainable feedstocks for future fuels, chemicals, polymers and fibres. Therefore materials research is ever more focused on the production of green or bio-based materials and their composites. Lignocellulosic biomass has become the feedstock of choice for these new materials as cellulose and lignin are the most abundant biopolymers on the planet. Lignin is a phenolic macromolecule, the principal biological source of aromatic structures, with a complex structure which varies depending on plant species and its isolation process. Despite its high carbon content and its potential as a raw material, lignin remains underutilised. Between 40 and 50 million tons of lignin are produced worldwide per year; while some is being used for low- and medium-value applications, most is

currently treated as a non-commercialized by-product or as low value fuel to produce energy. However, with the emergence of biorefinery projects larger amounts of lignin with the potential for valorisation are being produced. Here, we summarise some of the latest developments in the field.

*Keywords:* lignin; blends; composites; applications

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## 1. Introduction

Lignin is a functional polymer with relatively low molecular weight, and it represents a valuable biobased source for wide ranging applications [1-4]. It is the second most abundant polymer on the planet, is environmentally friendly, biodegradable, exhibits antioxidant properties, and displays antimicrobial activity. Interestingly, lignin is also being used as reinforcement for composite materials both in its natural fibre form and as a potential precursor for carbon fibre [5]. This review focuses on the valorisation of lignin in blends and its role as reinforcement in composites.

Lignin has been subject of previous reviews focusing on improvments of in its processability and relationships between the lignin structure and applied catalytic processes for its sustainable conversion into valuable products for applications in areas such as bioengineering [6-8], while another review focuses on value added applications involving micro- and nanostructured lignin [9].

However, this review is focused on the valorisation of lignin in advanced engineering materials. Section 1 briefly presents the main methods used for lignin separation from lignocellulosic resources. Section 2 describes the fractionation of lignin with its associated processing advantages. The third section summarises the most pertinent lignin blends with syntehic and biobased polymers. The fourth section is dedicated to the latest understanding of the role of lignin as a matrix, filler and reinforcement material in composites. Particular attention is paid to the promise of lignin as a precursor for carbon fibre and how its complex chemistry can be unravel unique biobased fibres. The fifth section details the importance of lignin in the realisation of latest strategies for the application of biobased macromolecules. Finally, we provide our outlook for the role of lignin in a post fossil based bioeconomy.

## 2. Lignin separation from lignocellulosic sources

Lignin extraction is technically challenging. Lignin can be isolated from various lignocellulosic sources (wood – softwood and hardwood species; crop, fiber and seed fibers plants – sugarcane, flax, jute, hemp, cotton; grasses, agricultural residues – rice and wheat straws, corn stover) but this has proven to be challenging as it is naturally resistant to chemical and enzymatic degradation. Figure 1, summarises various industrial and lab-scale separation methods. Here we summarise important sources of technical lignins which are likely to produce engineered materials, for more in-depth analysis on this topic the reader is referred to recent reviews [6-8].

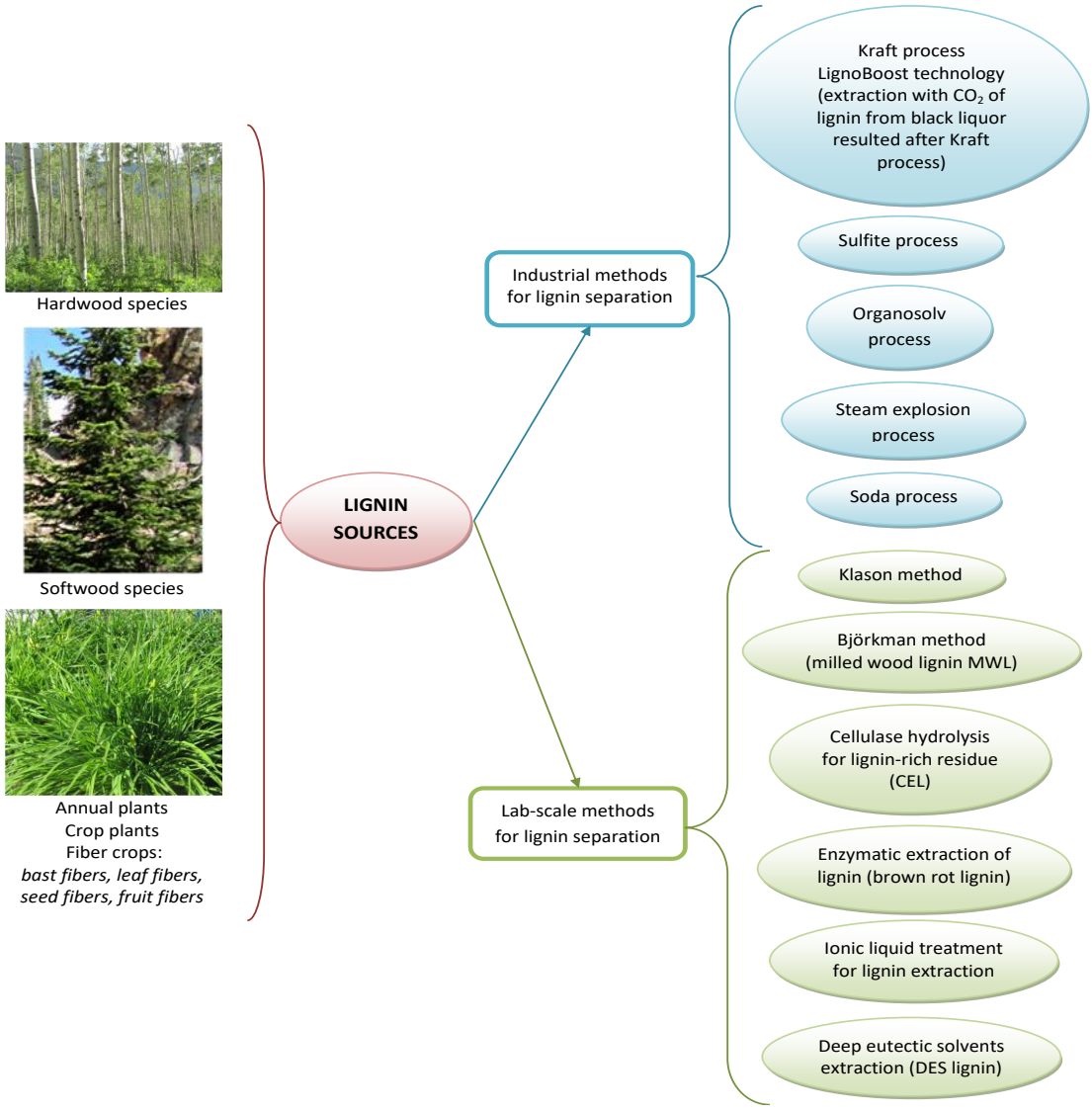

Figure 1. Schematic representation of the methods used for lignin separation from different lignocellulosic sources

The pulp and paper industry represents the main source of commercial technical lignin, resulting from processes such as:

- *alkaline pulping*: otherwise known as the Kraft process involves treatment of wood fibres in a 1 M NaOH and 0.25–0.70 M $Na_2S$ aqueous solution at 165-175°C. Depolymerisation proceeds through the cleavage of non-phenolic β–ethers and then through entrapment of quinone methide intermediates. The latter mechanism is an important improvement over the soda pulping process (NaOH only), which prevents additional condensation by formation of styryl ethers and diphenylmethane structures. However, sulphide introduces significant sulphur content into the Kraft lignin, and this impedes the subsequent valorisation of lignin. The Kraft process leads to replacement of C-O bonds of native lignins with C-C bonds inducing higher bond dissociation energies. Black liquor, contains highly complex and cross-linked lignin, is incinerated to recover $Na_2S$ and to produce steam for power generation.

- *organosolv processes*: allows the relatively easy separation of high purity lignin at elevated temperatures using a mixture of an organic solvent (i.e., ethanol, methanol, acetone, cyclic ethers or organic acids such as acetic acid and formic acid, or combinations chosen based on their ability to dissolve lignin), and water, in the presence of acid as catalyst (added or formed in-situ from hemicellulose fraction); the most well known are: Organocell process, Alcell process, CIMV process, Chempolis process, and the AST process;

Typical organosolv treatment involves pulping of wood chips (1 part solid for 4 to 10 parts liquid) at 180-195ºC in a solvent/water solution at 35-70%wt/vol at with or without acidic catalyst. The lignin, recovered by precipition, has a high degree of purity: it is sulphur-free with low carbohydrates and ash content. Organosolv lignins are readily soluble in organic solvents

however, this leads to lignin with a high level of α-O-4 and β-O-4 cleavages while the biphenyl 5-5 content is increased, affecting the reactivities of the lignin.

One of the best known organsolv lignins is Alcell lignin (from the ethanol based process) and it is expected that once these lignins are valorised to high end applications such as for example carbon fibres, the level of investment required for the implementation of the organosolv process at scale will be justified.

- *acidic pulping*: consists of sulfite processing using excess aqueous (bi)sulfite together with either sodium-, magnesium-, calcium- or ammonium hydroxide; the lignin is dissolved in the pulping black liquor as lignosulfonate, which is seperated from the other types of technical lignins, through water solubility.

- *steam explosion process*: involves pre-treatment of lignocellulosic sources with steam at about 200 °C or higher and high pressure for a short period of time followed by a rapid decompression; lignin is extracted from exploded fibrous material with either aqueous alkali or an organic solvent.

The majority of these processes induce extensive degradation of the native lignin structure. The best-known isolated lignin at lab-scale is Klason lignin, which is obtained by treating wood with sulfuric acid, the lignin is recovered as an insoluble residue after hydrolysis of polysaccharides (cellulose and hemicelluloses) to water-solubel sugars. This method for lignin isolation is usually used as an analytical means of determining lignin content, but generates a highly condensed and altered lignin, which it is unsuitable for chemical characterization or further chemical investigation. The most appropriate lignin for chemical and biological studies is considered to be milled wood lignin, which is most representative of lignin in the original lignocellulose source, namely protolignin.

Some recent extraction methods involve the use of advanced solvents for selective dissolution of lignocelluloisc components; these include ionic liquids (IL's) and deep eutectic solvents (DES) specifically for delignification and further valorization of isolated lignin.

## 3. Lignin fractionation

The variety of cross-linkages possible between the lignin chain units makes it highly heterogenous and has been found to be challenging for its valorization [6,10]. Fractionation is a physico-chemical modification technique, which enables the separation of high molecular weight lignin chains from lower molecular weight fractions in isolated technical lignin (see Figure 2). Fractions can be separated by partial suspension in organic solvents, enzymatic treatment [11,12], selective precipitation at reduced pH and membrane assisted ultrafiltration [13,14]. Both enzymatic and ultrafiltration methods control effectively molecular weight distribution of lignin, but the techniques are costly and difficult to upscale to an industrial level [15]. All types of technical lignins have been investigated for their fractionation; however, softwood Kraft lignin is the most commonly fractionationed lignin. Recent work from Dodd and Kadla has shown that two softwood kraft lignins of different origin (southern pine and Norwegian spruce) have major chemical and physical differences despite the same extraction technique [16]. However, characterization studies showed that fractions obtained from lignins of different origins follow similar trends with regards to their chemical and physical properties [17-19].

The solvent fractionation technique was first reported in 1941 by Lovell and Hibbert [20]. Methods can use one or multiple organic solvents to separate the fractions with different molecular weight, thermal properties and chemical structures [21-23]. Using a sequential approach with solvents of different polarity enables to tune the properties of the fractions obtained, by either dissolution of the insoluble fractions in successive solvents, with increasing solubility parameters [24-26], as developed by Mörck for Kraft lignin [17-19] or by

precipitation of the soluble fraction by using solvents with decreasing solubility parameters [17-19,23,27-32]. All studies show that the fractions have a lower polydispersity than the "as received lignin". The molecular weight of the fraction modulates its thermal and structural properties: higher molecular weight fractions have a higher $T_g$ and higher char yield, higher number of aliphatic OH and lower number of phenolic OH than the low molecular weight fractions which has lower thermal resistance [30,33]. $^{31}$P NMR studies showed that the alkyl ether linkages are replaced by C-C linkages in the low molecular weight fractions while the high molecular weight ones are enriched in β-O-4' linkages [25,29]. The modulation of the number of phenolic OH by solvent fractionation was used for improving antioxidant properties for polyurethane production [30,33] and antimicrobial activities [34,35]. Chemical protection of the hydroxyl groups in phenolic enriched softwood Kraft lignin fractions enabled Argyropolous *et al.* [36] to synthesize lignin-poly(arylene ether sulfone) copolymers. In a similar approach, methylated lignin fractions blended with polyethylene showed improved melt spinning abilities of the softwood kraft lignin [37]. Gregorova and Sedlarik found that kraft lignin successively dissolved in dichloromethane and methanol has increased heavy metal scavenging activity [38]. A lignin-based concrete water reducer was developed based on sulfonated lignin fractionned with acetone [39]. Kraft lignin fractions have been investigated as carbon fiber precursors [10,40]. Fractionation has been used as a pretreatment to separate different molecular weight groups for lignin monomer production by catalytic depolymerisation using supercritical ethanol and ruthenium catalyst supported on activated carbon [41]. Perez used water and ethyl acetate to separate depolymerization products after supercritical water oxidation [42].

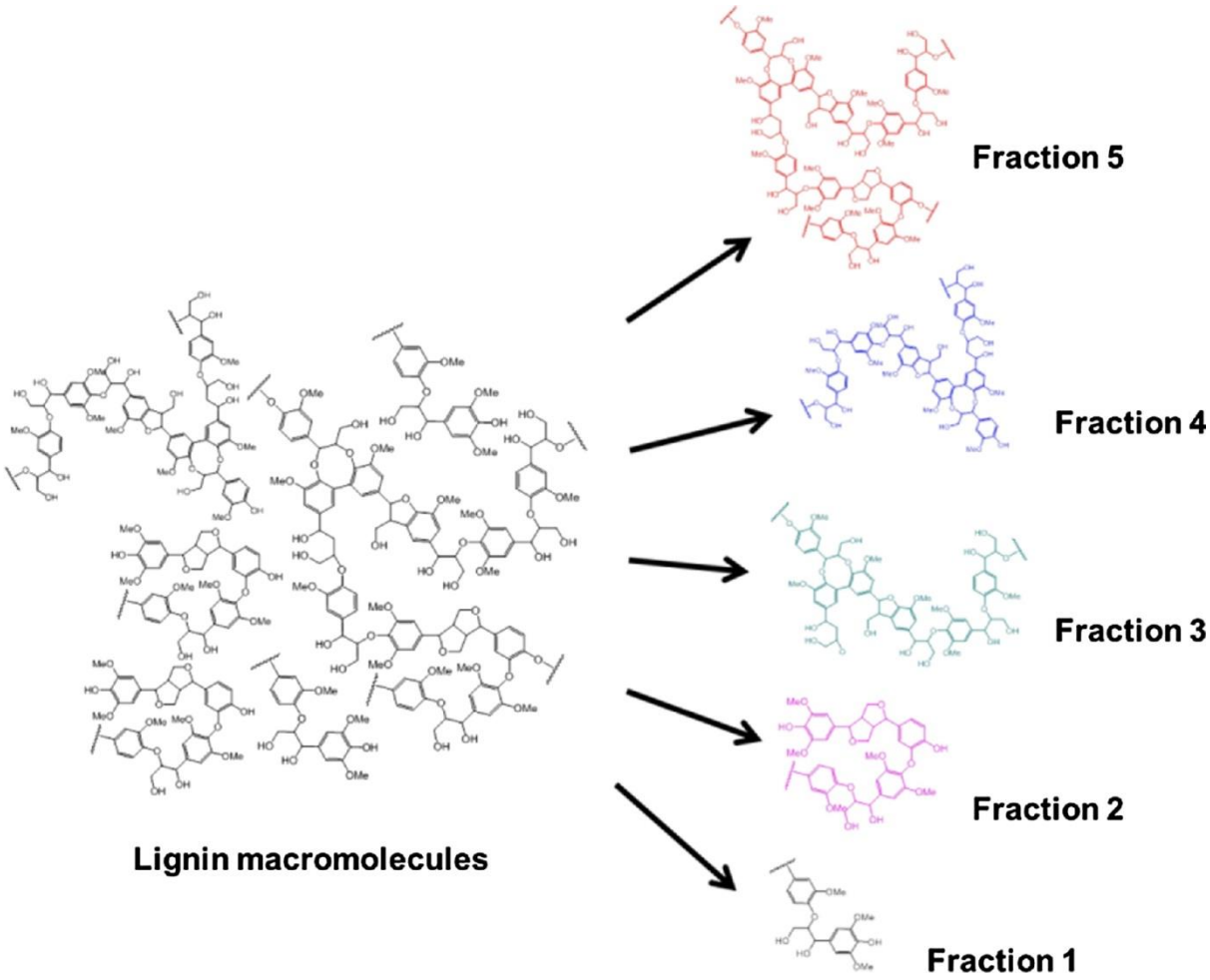


Figure 2. Separation of lignin by sequential fractionation, reproduced with permission from [25]

**4. Lignin-polymer blends**

Lignin has been blended with a number of polymers in order to obtain materials for high added-value applications. Efficient blending is often difficult to achieve considering the high complexity of the lignin structure and its reactivity. Lignin manifests thermoplastic behavior due to its network of strong intra- and inter-molecular hydrogen bonds [43, 44], but at high temperatures it acts as a thermoset material through occurrence of extensive cross-linking reactions [5,45]. In this context, it is of critical importance to thoroughly investigate lignin miscibility with other polymers, monitoring the evolution of phases as their compatbility or

otherwise is of real importance in gaining an undertsanding of the structure property relationships of lignin based blends [46].

Depending on the compatibility between lignin and different polymer matrices, the resulting blends can either form miscible blends or display a phase separation. Lignin, a relatively polar polymer due to its numerous structural OH groups, generally presents a high affinity toward polar polymer matrices. Miscible blends were observed in Kraft lignin with poly(ethylene oxide) (PEO) and poly(ethylene terephthalate) (PET) blends, while immiscible blends were found in Kraft lignin with poly(propylene) and poly(vinyl alcohol) (PVA) [47]. The compatibility in lignin blends can be evaluated by the blend morphology, investigated through visible microscopy and by assessment of lignin solubility, its concentration being determined by measuring UV absorbance of microtome section in homogeneous areas through UV microspectrophotometry methods [48].

The major drawbacks of lignin usage as an amorphous thermoplastic component in the formulation of various polymer materials is associated with its relatively high glass-transition temperature and, consequently, by its difficulty to process through thermal blending routes, when lignin undergoes self-condensation reactions through extensive cross-linking and strong intramolecular interactions under high temperature conditions, leading to inherent brittleness. Normally, these processing issues can be overcome through the blending of lignin with synthetic polymers (including co-polymerization approach) [1], biopolymers [2], through the utilization of plasticizers [3], or through chemical modification techniques [49,50].

Lignin is effective as an antioxidant and for UV protection due to its radical scavenging ability. Therefore, it is often blended with polymers such as polyethylene, PE and polypropylene, PP) to improve their thermal oxidative resistance [51]. Lignin depolymerization, is often utilised to improve compatibility with the polymer matrix through decreasing its molecular weight, increasing phenolic content, and reducing aliphatic hydroxyl content [52, 53]. Lignin

depolymerization with selective bond cleavage is also performed in order to minimize lignin condensation which can often limit the conversion of lignin into value-added products [54-56].

Table 1 provides examples of lignin blends with different synthetic polymer matrices, biopolymers and other polymer systems.

**Table 1.** Blends of lignin with different polymer matrices

| Blend type | Polymer matrix | Example of blend | Type of lignin | Reference |
|---|---|---|---|---|
| *lignin-synthetic polymers blends* | thermoplastic polyolefins | polyethylene PE | industrial lignins (hardwood and softwood Kraft lignins, softwood organosolv lignin, wheat straw soda lignin, hydrolysis lignin from wheat) | [57] |
| | | | LignoBoost softwood Kraft lignin; hardwood Kraft lignin | [58,59] |
| | | | softwood Kraft lignin | [60] |
| | | | hardwood lignin from prehydrolysis of beech | [61] |
| | | polypropylene PP | softwood Kraft lignin | [62] |
| | | | liquid wood (Arboform) – a mixture of lignin (30%), cellulose from hemp and flax (60%), natural additives | [63] |
| | | | Kraft lignin from sugarcane bagasse, hardwood Kraft lignin | [64-66] |
| | | | softwood lignosulfonates | [67] |
| | | | softwood kraft lignin | [68] |
| | | | industrial waste lignin from bagasse | [69] |
| | | | hardwood lignin from prehydrolysis of beech | [61] |
| | polyolefin elastomers | maleic anhydride grafted copolymers of ethylene propylene rubber EPRs | softwood lignosulfonate | [70] |
| | | ethylene propylene diene monomer rubber EPDM | pure and undegraded lignin from wheat straw (CIMV organosolv process) | [71] |
| | synthetic rubber | styrene-butadiene rubber | hardwood soda lignin (sulfur free lignin) | [72] |
| | acrylate monomers | butylmethacrylate BMA | biobutanol lignin from agricultural wastes (corn stalks and wheat straw) | [73] |

| | | | | |
|---|---|---|---|---|
| | vinyl polymers | poly(vinylacetate) PVAc | acetone-soluble lignin fraction of sugarcane bagasse (organosolv lignin) | [74] |
| | | poly(vinyl chloride) PVC | softwood Kraft lignin;<br>softwood lignosulfonate;<br>hardwood lignosulfonate<br>hardwood organosolv lignin | [75]<br><br><br>[76-78] |
| | | poly(vinyl alcohol) PVA | hardwood Kraft lignin<br>hardwood Kraft lignin | [79]<br>[80] |
| | polyesters | polyethylene terephthalate PET | hardwood Kraft lignin | [66] |
| | | polylactic acid PLA | organosolv lignin from wheat straw<br>softwood organosolv lignin<br>softwood Kraft lignin;<br>organosolv lignin from almond shells;<br>softwood Kraft lignin | [81]<br><br>[82]<br>[83-85] |
| | | polycaprolactone PCL | soda lignin from wheat straw<br>steam explosion lignin from wheat straw; softwood lignosulfonate<br>softwood sodium lignosulfonate | [86]<br><br>[87,88]<br><br><br>[89] |
| | | polyhydroxybutyrate PHB | soda lignin from sugarcane bagasse<br>softwood sodium lignosulfonate | [90-92]<br><br>[93] |
| | | polybutylene succinate | softwood lignosulfonate<br>softwood Kraft lignin | [94]<br>[95] |
| | polyether | polyethylene oxide PEO | softwood Kraft lignin<br>hardwood Alcell lignin | [96]<br>[97] |
| | thermoplastic elastomer | polyurethane | hardwood organosolv lignin; hardwood Kraft lignin<br>eucalyptus wood Kraft lignin, softwood and hardwood Kraft lignins | [98]<br><br><br>[99] |
| | | poly(N-vinyl pyrrolidone) | organosolv lignin from annual plants<br>soda lignin from sugarcane bagasse | [100]<br><br>[101] |
| | | polyacrylonitrile PAN | soda lignin from wheat straw | [102] |
| | polyamides | polyamide 6 (nylon 6) | soda lignin from mixed wheat straw/Sarkanda grass | [103] |
| | | polyamide 11 (PA11) | soda lignin from annual plants (sisal and abaca), hardwood organosolv lignin | [104] |

| | | | | |
|---|---|---|---|---|
| | | polyaniline | hardwood Kraft lignin | [105] |
| | | polystyrene | softwood lignosulfonate<br>softwood Kraft lignin | [106]<br>[107] |
| | | poly (4-vinylpyridine) | alkali lignin from bamboo | [108] |
| | | poly(ester-amine) | soda lignin from mixed wheat straw/Sarkanda grass | [109] |
| | co-monomers | poly(butylene adipate-co -terephthalate) PBAT | soda lignin from mixed wheat straw/Sarkanda grass | [110] |
| | | poly(hydroxybutyrate-co-hydroxyvalerate) PHBV | softwood Kraft lignin<br>soda lignin from steam-exploded sugarcane bagasse | [111]<br>[112] |
| *lignin-biopolymer blends* | proteins | fish proteins | softwood Kraft lignin | [113] |
| | | wheat gluten | softwood Kraft lignin | [114] |
| | | soy protein | Kraft lignin from bamboo | [115] |
| | polysaccharides | starch | softwood Kraft lignin<br>hardwood Klason lignin (acid insoluble lignin)<br>LignoBoost softwood Kraft lignin<br>soda lignin from wheat straw and bagasse; lignosulfonates from mixed hardwoods | [116]<br>[117]<br>[118]<br>[119]<br>[120] |
| | | cellulose | softwood Kraft lignin<br>ionosolv lignin from willow crop<br>organosolv/Kraft lignin from eucalyptus wood | [121]<br>[122]<br>[123] |
| | | chitosan | softwood Kraft lignin<br>soda lignin from wheat straw ( sulphur-free anionic sodium carbonate lignin) | [124]<br>[125] |
| | | gelatin | soda lignin from annual plants<br>lignosulfonate from eucalyptus wood | [126,127]<br>[128] |
| *other polymer systems* | | poly(butylene-adipate-co-terephtalate)–polylactide–lignin (PBAT–PLA–Lig) | softwood Kraft lignin | [129] |
| | | poly(ethylene-co-vinyl alcohol) | softwood lignosulfonate | [130] |

| | | | | |
|---|---|---|---|---|
| | | glycol modified poly(ethylene terephthalate) PETG | softwood lignosulfonate | [131] |
| | | polycarbonate | softwood lignosulfonate | [131] |

To achieve better properties in lignin-polymer blends, chemical modification of lignin is often required [59, 60, 63, 82, 107, 115, 116]. In general, lignins, neat or chemically modified, could be used to fulfill the following functions within a blend system: reactive component in the preparation of various resins (e.g. epoxy resins, phenol formaldehyde resins (section 6.2) [132,133]) and polymers (e.g. polyurethanes (sections 4 and 5.2) [98,134-136]), nucleating agent (section 4) [86,93,94,137], surfactant [138-141], UV blocker (section 4) [51,110,142-145], thermal stabilizer (section 4) [52,53,62,146], flame retardant [147-152], adsorbing agent (section 4) [124], reinforcing filler in composites (section 5) [60,62,71,72,94,95,137,153], anti-microbial agent (biocide) [154,155], supercapacitor for energy storage (section 6.3) [156-159], carrier (for biomedical and pharmaceutical applications) (sections 4 and 5.3) [121,160], and precursor for sustainable and cost-effective carbon fibers (section 5.4) [161].

## 5. Lignin in composite formulations

Considerable efforts have been made in recent decades in order to valorize lignin and its derivatives into advanced composite materials driven by the accelerated fossil reserves depletion, increased environmental awareness, and the high societal demand for eco-friendly, renewable, self-sustainable materials as well as governmental incentives and legislation [162]. A wide variety of applications is already known and well documented, ranging from simple formulations up to multicomponent/multifunctional polymeric systems with tunable property capability [163]. Therefore, extensive research has been dedicated to elucidate the structure/property relationships in lignin, as well as its interactions with other materials

[164,165]. These studies have enabled the usage of lignin-based materials in advanced applications, such as bioplastics for agricultural purposes (e.g. lignin-based mulch films) and food packaging [166-168], and slow-release fertilizers and herbicides [169,170], such materials being also valuable for the production of biofuels [171-175], energy storage devices [176,177], structural modifiers [82,168,178-184], nanocomposites, nanoparticles and nanofibers [185-191].

However, the literature is inconsistent in its definition and classification of lignin-based multicomponent materials. With the terms ”blends” and ”composites” used interchangeably, while the role of lignin itself is often uncertain: varying between a matrix material, or an additive; either as a filler or reinforcement. In the subsequent sections we attempt to clarify these issues.

### 5.1 Lignin as matrix for composite materials

Since the melting temperature of lignin is in the range of 140-160°C (lower than PLA: 180-210°C) [184] and given its complex thermal behavior, it is well suited as a matrix for thermoplastic biocomposites which contain natural thermo-sensitive fillers/reinforcements, such as hemp, flax, and wood to produce fully biobased composites or green composites [192-200]. Results have shown that effective bonding between the lignin matrix and natural fibers is possible [184]. Such composites display mechanical properties which are highly dependant on fiber content, but above certain amounts of filler these properties were significantly reduced [201]. Along with weight reductions and less shrinkage, these materials proved to be effective in the attenuation of sound and noise, and oscillations [202], as well as shock absorbance [184], and are thermally stable at high temperatures not requiring flame retardants [203]. When metal nanoparticles (Pt) were deposited onto natural fibers (softwood, hemp) and subsequently incorporated into the lignin matrix, composites with reduced electrical resistance were produced [204-207]. Combining the properties of different fillers, such as natural fibers and

clays (sepiolite, organically modified Montmorillonite (MMT), it is possible to obtain lignin-based thermoplastic composites with predetermined properties in terms of mechanical and thermal performance [208].

### 5.2 Lignin-containing composites

Generally, it has proven difficult to incorporate high amounts of raw lignin (up to 40% w/w) into composite matrices, due to its poor compatibility, however lignin derivatives have shown promise. Thus, using Kraft lignin, it is possible to increase the content up to 80 wt%, and, consequently, significantly improve the tensile strength and Young`s moduli of matrices [163].

Composites containing different types of lignin fillers (Kraft, organosolv, soda lignin, acetylated softwood Kraft lignin - ASKL) have proven to display high performance properties [87,163]. Experimental data has confirmed that lignin addition increases the crystallization rate and degree of crystallinity, improves thermal properties (i.e., enhanced flame retardancy due to the formation of high amounts of char residue upon heating in an inert atmosphere, which reduces the combustion heat and the heat release rate), and enhances mechanical properties of matrices as shown in Table 2.

**Table 2.** Thermoplastic composites containing lignin as filler

| Matrix | Lignin type | Observations | Ref. |
|---|---|---|---|
| PP | from wood | use of 2% reactive compatibilizer with flexible segment (RCFS) | [209] |
| | | compatibilized with a hyperbranched polymer lubricant (HBPL) | [210] |
| | from wood | less loss of flexural strength and modulus and less roughness on the weathered surface | [211] |
| | | impact properties improved | [212] |
| | | modification of surface properties: polypropylene surface achieved increased hydrophilicity | [213] |
| | hardwood Kraft lignin | main objective: improving the strength properties of the composites; lignin surface modification depends on the nature of the plasma treatment: $SiCl_4$-plasma treatment resulted in silicon implantation; plasma-induced copolymerization of acryloyl chloride on lignin yielded in thin film deposition. | [214] |

| | | | |
|---|---|---|---|
| PE | hardwood Kraft lignin | free-radical grafting as a compatibilization method | [215] |
| | | different compatibilizing agents (PE-a-MAH and PP-a-MAH) were added to improve the interfacial interactions between matrix and filler; PE-a-MAH proved to be more effective for the PE-based composites | [216-219] |
| | | MA-g-LDPE as compatibilizer and copper(II) sulfate pentahydrate (CuSO4.5H2O) as dispersing agent for lignin in PE | [220] |
| | | catalytic grafting technique of lignin particles to PE | [221] |
| | | various contents of lignin (1-15%); antibacterial activity increased | [222] |
| | | addition of EVA as compatibilizer and a transition metal salt as oxo-biodegradation promoter | [223] |
| | | foams with mixed matrix LDPE-EVA and lignin particles homogeneously dispersed | [224] |
| PS - key issue: lack of compati-bility between components, leading to poor properties | | content of lignin 0%-80%; addition of a compatibilizer | [107] |
| | | content of lignin 0%-80%; addition of a compatibilizer | [225] |
| | lignin from rice straw pulp | lignin complexation with cobalt (II); potential applications in the area of marked packaging materials | [226] |
| | | the matrix was grafted on the lignin nanoparticles; the formation of aggregates was observed, indicating incompatibility between the lignin particles and the PS; nanocomposites with a tailored architecture can be obtained | [227] |
| PA | Alcell (organosolv lignin from abaca and sisal | PA11 derived from castor oil; lignin particles remained well-dispersed in the polyamide matrix | [102] |
| | organosolv lignin | PA6; lignin content prevented degradation of the composite (susceptibility of PA to UV radiation) | [228] |
| PVC | lignin treated with poly(ethyl acrylate-co-maleic anhydride) | the pretreatment of lignin resulted in improved toughness and impact strength | [229] |
| | lignin treated with poly(ethyl acrylate-co-acrylic acid) | improved thermal properties | [230] |
| | lignin with a lower molecular weight resulted by fractioning in a mixture of propanol, ethanol, and methanol | although lignin can be compatible with the PVC matrix, its rigid phenolic structure results in increased brittleness | [231] |

| | | | |
|---|---|---|---|
| | lignin particles treated with polyacrylate | improved compatibility | [232] |
| | magnesium hydroxide-functionalized lignin | filler content 2.5-10%; notable fire resistance of composites | [233] |
| | $SiO_2$–lignin particles | filler content 2.5-10%; notable fire resistance of composites | [234] |
| PVA – main issue: to reduce miscibility | lignin nanoparticles obtained using a high-shear homogenizer | a slight increase in the thermal stability | [235] |
| | quaternized lignin | use of a formaldehyde as cross-linking agent to increas the water resistance | [236] |
| | quaternized lignin | the adsorption was strongly influenced by pH | [237] |
| ABS | | reactive compatibilization; improved flame resistance of the composite | [238] |
| TPU | ASKL | lignin content: up to 90%; the phase morphology changed from an isolated hard domain structure to an interconnected one as the physical cross-links increased | [239] |
| starch | Kraft lignin and esterified lignin | improved mechanical properties and resistance to water sorption | [116] |
| poly-siloxanes | | polydimethylsiloxane improved the water sorption resistance | [240] |
| | mixed filler: lignin as a bulky filler and silica | polysiloxane matrix was less compatible with lignin than silica, and a phase separation occurred yielding in a composite with a surface rich in hydrophobic units | [241] |
| polyaniline | | removal and recovery of Au(III) from aqueous solutions; low-cost lignin-based biosorbent | [242] |
| silica | | silica matrix; porous structures for the sorption of heavy metals | [243] |
| | | hydrated silica matrix; preliminary silica modification entailed an increased surface activity, yielding in binding a greater amount of lignin at the same weight contributions; confirmed their mesoporous structure | [244] |
| poly(*o*-phenylene diamine) | | formation of lignin-based composites on the surface of a glassy carbon electrode, due to electrochemical properties of the composite | [245] |
| PET | | lignin content up to 20%; lignin prevents the oxygen transfer toward the polymer | [246] |

The ideal multicomponent system for a thermosetting formulation requires the components to have a low viscosity prior to curing, and, therefore, it is of critical importance to find the best

suited materials (for example, unsaturated polyester resins for glass-fiber composites, epoxy resins for carbon fiber composites). Given its highly branched structure, functional groups, and free positions for substitution at the aromatic nuclei, lignin can be considered a valuable component in both thermosetting resins (as component or replacement of the hydroxylic co-monomer) and thermosetting composite formulations. Even more so, as the type of lignin influences the final properties of the material; thus, different types of lignin, including Kraft lignin (KL), lignosulfonates, organosolv and enzymatic hydrolysis lignins, have been studied in these systems [247].

The main characteristic of lignin in such complex formulations is its reactivity: lignin behaves as a reactive filler. Athough the vast majority of work has been on the addition of lignin to thermosetting resins, recent studies have reported lignin as filler in thermosetting composite formulations [2].

Most common thermosetting resins used for lignin-containing composites are phenol-formaldehydes (PF), polyurethanes (PU), and epoxies (EP). In PF formulations, lignin was predominatly employed as resin component. However, when it is used for highly porous aerogels and cryogels containing over 80% lignin [248], it has been reported that lignin acted as both a resin component and reactive filler. Enzymatic treatment of lignin activates the phenolic rings of its structure by oxidation and this lignin modification may be employed in urea-formaldehyde-based composites [249]. It has been reported that lower amounts of resin were used as a result of lignin acting both as filler and binder. It has been shownthat 3% lignin in a PU-based composite formulation, where the PU was made of hydroxyl terminated polybutadiene as soft segment in combination with toluene diisocyanate (TDI), yielded materials with poor mechanical properties because some of the lignin remained unreacted and behaved as filler, thus causing an irregular network structure [250,251]. A similar behaviour was ascertained for lignin in some rigid [252] and flexible PU foams (made of softwood Kraft

lignin, PEG with variable molecular weights and TDI) [253]. In the case of flexible foams, it was concluded that the viscoelastic properties of the foams is highly dependent on the increasing hard segment content as the lignin component is acting as a filler, and limiting crosslinking effects. A PU-based sealant containing various amounts of lignin (5-20%) has also been reported and it showed increased toughness and stiffness depending on the lignin content as it partly acted as reinforcement [254].

### 5.2.1 Lignin reinforced bioplastic composites

Lignin-reinforced biocomposites can be processed in extruders with modified geometry to allow good distribution of filler and prevent thermal degradation of both matrix and reinforcement components. At the same time, given that lignin is commercially available as particles or powder, other methods, such as heating-cooling mixing or extrusion-compression molding, can also be employed. Most of these biocomposites show improved thermal and mechanical properties, and can be used in odor and emission control as well. A few examples are presented in Table 3.

**Table 3.** Lignin as filler in biocomposites

| Biopolymer matrix | Comments | Ref. |
|---|---|---|

| | | |
|---|---|---|
| polybutylene succinate (PBS) | methylene diphenyl diisocyanate (PMDI) compatibilizer; lignin weight content: 65 % | [255] |
| | lignin and switch grass as reinforcement; polymeric methylene diphenyl diisocyanate (PMDI) as compatibilizer | [256] |
| | filler: acidolysis lignin and alkali enzymatic lignin | [257] |
| | WAXD and SAXS investigations revealed that presence of the AL does not influence the crystal and supermolecular characteristics of the PHB | [258] |
| poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) | lignin was obtained from sugar cane bagasse; lignin content up to 80% | [112] |
| starch | reactive filler; lignin stabilizes the residual starch structure | [259] |
| | mixed matrix: cellulose and starch; lignin filler (1-5 wt%); hybrid green composite films with excellent mechanical properties in dry and wet states, and good thermal stability and high gas barrier | [260] |
| | matrix: glycerol-plasticized corn starch (GCS) – adipic acid modified starch microparticles (AASM) | [261] |
| PA | tall oil based polyamide | [283] |
| polybutylene adipate-*ω*-terephtalate | applications: non-food packaging or other short-lived applications (agriculture, sport) | [262] |
| PLA | PEG added as plasticizer | [263] |
| | three silane coupling agents: 3-aminopropyltrieethoxy-silane, γ-glycidoxypropyl-trimethoxy-silane, and g-methylacryloxy-propyltrimethoxy-silane | [264] |
| | composites exhibited a six-fold increase of elongation at break and a simultaneous improvement in their tensile strength and Young's modulus | [265] |
| | comparative study using PP or PLA as matrix, and cellulose, lignin or wood flour as filler | [266] |
| matural rubber (NR) | NR/soda lignin and NR/thiolignin composites | [267] |
| | improvement of main mechanical properties | [268] |
| | comparative study on natural rubber (NR) and styrene butadiene rubber (SBR) matrices; lignin filler -forming agglomerates | [269] |
| | epoxidized natural rubber | [270] |
| | homogeneous dispersion of filler and the strong interfacial adhesion significantly enhanced the thermal stability and mechanical properties of nanocomposites | [187] |

### 5.3 Lignin in nanocomposite materials

In an effort to further valorise lignin, it has been successfully converted into nanoparticles, nanocapsules, nanofibers, nanotubes and other nanostructured materials [190,271-273] and

these nanomaterials are finding application in the biomedical sector (gene therapy, controlled drug release, pharmaceutical excipients [274]), food packaging, UV protection, as antioxidants, and in microfluidics [275].

Lignin nanoparticles significantly improve the thermal and mechanical properties of their corresponding polymer nanocomposites. The presence of reactive functional groups on the nanoparticle surface, enables surface modification reactions which can contibute to the interfacial adhesion between the nanofillers and matrix material. Lignin nanoparticles can be obtained by differing methods antisolvent precipitation, interfacial crosslinking, ultra-/sonication, polymerization, solvent exchange, and so on, the resulting particles may have predefined shapes, size and dimensional distribution. Some recent developments in the field of nanostructured lignin-based materials are presented in Table 4.

**Table 4.** Lignin-based nanostructured materials

| Nanostructured material | Comments | Ref. |
|---|---|---|
| nanoparticles | solid and hollow spherical lignin nano- and microparticles using ultrasonic spray-freezing and electrostatic stabilization; applications: cosmetics (sunscreen), pharmaceutics (drug delivery) | [276] |
| | nanoparticles obtained by gradually addition of HCl to lignin solutions in ethylene glycol; no cytotoxicity towards yeast or microalgae | [277] |
| | addition of water (non solvent ) to a solution of acetylated lignin in THF | [278] |
| | lignin alkaline solutions were added to cationic polyelectrolyte solutions of poly(diallyldimethylammonium chloride); colloidal particles (200 nm diameter) with a positive surface charge were obtained | [187] |
| | lignin nanoparticles as antioxidants and UV protection | [144] |
| | core-shell silver-lignin nanoparticles | [279] |
| | organic-inorganic hybrid materials containing lignin nanoparticles | [280] |
| | one pot synthesis of lignin nanoparticles in the presence of liquid $CO_2$ as antisolvent | [281] |
| | lignin micelles for UV protection | [282] |
| | Pickering emulsions stabilized by lignin nanoparticles | [283] |
| | hyperbranched lignin copolymers able to self organize as to form nanoparticles with plasmid DNA (pDNA); promising nonviral gene vectors gene delivery applications | [284] |

| | | |
|---|---|---|
| | lignin nanoparticles obtained by ultrasonication | [285] |
| | introducing water into the solution of softwood kraft lignin in tetrahydrofuran (THF) through dialysis | [286] |
| | lignin-based nanoparticles for antitumoral drug delivery | [188] |
| | organic –inorganic hybrid nanoparticles of lignin treated with iron isopropoxide | [287] |
| | lignin nano- and microparticles for stabilized emulsions | [288] |
| | polyacrylamide-g-kraft lignin nanoparticles were obtained using reversible addition–fragmentation chain transfer (RAFT) method; application: Pickering emulsions (tuning the aggregation strength while retaining interfacial activity) | [289] |
| | enzyme-assisted preparation of lignin nanoparticles (20-100 nm) with reduced polydispersity | [290] |
| | uniform size and shape nanospheres obtained by self-assembly of enzymatic hydrolysis lignin (EHL) dissolved in tetrahydrofuran by adding water under magnetic stirring | [291] |
| | lignin nanoparticles in PVA and chitosan formulations were tested for their biocide properties; applications: food packaging, drug delivery, tissues engineering, wound care | [292] |
| | lignin nanoparticles in PLA and PLA-g-GMA matrices as weathering protection and UV barrier | [293] |
| nanofibers | PLLA/PLA–lignin electrospun nanofibers with excellent antioxidant activity and good biocompatibility for biomedical applications | [294] |
| | hybrid polyester-lignin nanofibers | [295] |
| | lignin-based electrospun nanofibers with highly elastic properties | [296] |
| | electrospun defect-free nanofibers from soy protein and lignin | [297] |
| | defect-free electrospun nanocomposite fibers produced from aqueous dispersions of PVA, lignin nanoparticles and cellulose nanocrystals | [298] |
| | lignin-based electrospun nanofibers reinforced with cellulose nanocrystals | [299] |
| nanocapsules | oil-filled capsules of kraft lignin synthesized from an oil in water emulsion submitted to a high-intensity, ultrasound-assisted crosslinking of lignin at the water/oil interface; nanocapsules (diameter 300 nm) were obtained when prepared in the presence of PEGDEG | [186] |
| | hollow nanocapsules (160-390 nm) obtained by interfacial polyaddition in inverse miniemulsions; the nanocontainers can be loaded with hydrophilic substances which can be released by an enzymatic trigger | [300] |
| | nanocapsules by self-assembly of Kraft lignin | [301] |
| | pH-sensitive lignin nanocapsules for controlled delivery of hydrophobic molecules | [302] |
| nanotubes | lignin nanotubes as smart delivery vehicles for DNA; no cytotoxicity associated; no immunogenicity as in the case of viral vectors | [303] |
| | hybrid fibers made of nanocomposites containing softwood kraft lignin and MWCNTs; good porosity and surface properties | [304] |
| | MWCNTs-lignin nanocomposites with redox activity | [305] |

| | | |
|---|---|---|
| other nanostructured materials | ternary nanocomposite films based on PLA and hybrid nanofillers: cellulose nanocrystals and lignin nanoparticles; application in food packaging | [306, 307] |
| | PMMA nanocomposites with lignin nanoparticles obtained by free-radical graft polymerization combined with masterbatch procedure | [308] |
| | graphene exfoliation and stabilization in the presence of lignin by adsorption of lignin onto graphene surface (hybrid nanosheets) *via* π-π interactions during ultrasonic processing | [309] |

Chemical modification of lignin based nanomaterials offers the possibility to open new directions for the development of lignin-based multicomponent polymer systems with tailored properties. Even more so, given their biocompatibility, lack of cytotoxicity, and biodegradability, lignin utilisation for biomedical applications, such as drug and gene delivery, cosmetics and pharmaceutics offers an intriging prospect.

In blend or composite/nanocomposite formulations, raw or chemically modified, in combination with synthetic/natural polymers, assisted by specific additives (compatibilizing agents, dispersants, flame retardants, enzymes etc.), lignin proved to beneficially add to the properties' performance of the resulted polymer systems. Recent applications of lignin in thermoplastic/thermosetting and natural rubber polymer systems are presented in Tables 5-7.

**Table 5.** Recent applications of lignin in thermoplastic polymer systems

| **Polymer matrix** | **Investigated properties** | **Lignin content** | **Ref.** |
|---|---|---|---|
| LDPE | mechanical and thermal properties | up to 40wt% | [60] |
| LDPE | mechanical properties and morphology | 20wt% | [310] |
| HDPE | UV weathering | 0-29wt% | [311] |
| HDPE | dimensional stability, morphology, thermal and mechanical properties | 20wt% | [312] |
| HDPE | density, morphology, mechanical and thermal properties | 40-60wt% | [313] |
| PP | mechanical and morphological properties | 50wt% | [314] |
| PP | morphology, mechanical and thermal properties | 30wt% | [315] |
| PP | mechanical, thermal and rheological properties, oxidation induction time | 10-30wt% | [316] |
| PP | physical, mechanical, and thermal properties | 50wt% | [182] |
| PP | mechanical properties, melting/crystallization behavior and morphology | 20-40wt% | [317] |
| PS | mechanical and rheological behavior | 0-80wt% | [107] |

| | | | |
|---|---|---|---|
| PS | morphological structure, thermal properties, mechanical properties | 5wt% | [317] |
| PS | mechanical and thermal properties | 3.2-19.6wt% | [225] |
| PS | thermal stability, mechanical properties | 0-80wt% | [226] |
| PET | supermolecular structure and thermal properties | 0-70 wt% | [318] |
| PET | thermal stability and melting behavior, crystallinity | 0-80wt% | [246] |
| TPU | mechanical and thermal properties, rheology | up to 90wt% | [319] |
| TPU | thermo-mechanical properties, thermal stability and dielectric properties | up to 30wt% | [320] |
| TPU | mechanical and thermal properties | 5-20 wt% | [321] |
| PDMS | mechanical and thermal properties | 0-70wt% | [241] |
| ABS | thermal, mechanical, and rheological properties | 10-30wt% | [322] |

LDPE= low density polyethylene; HDPE=high density polyethylene; PP= polypropylene; PS=polystyrene; PET=poly(ethylene terephthalate); TPU= thermoplastic polyurethane; PDMS=polydimethylsiloxane; ABS=acrylonitrile butadiene styrene

**Table 6.** Recent applications of lignin in thermosetting polymer systems

| **Polymer matrix** | **Investigated properties** | **Lignin content** | **Ref.** |
|---|---|---|---|
| Epoxy resin | mechanical properties | 15-30wt% | [323] |
| Epoxy resin | mechanical and thermal properties | 2-9wt% | [324] |
| Epoxy resin | mechanical, thermal and microstructure properties | up to 60 wt% | [325] |
| Epoxy resin | thermal stability, shear strength | 5wt% | [326] |
| Epoxy resin | tensile properties | up to 50 wt% | [327] |
| PFR | wettability, contact angles | up to 40 wt% | [328] |
| PFR | thermal properties | 5-20wt% | [329] |
| Poly(vinyl ester) resin | thermo-mechanical properties | 10-30wt% | [330] |

PFR= phenol formaldehyde resin

**Table 7.** Recent applications of lignin in rubber polymer systems

| **Polymer matrix** | **Investigated properties** | **Lignin content** | **Ref.** |
|---|---|---|---|
| SBR | mechanical properties | 20-30wt% | [331] |
| NR | thermal and mechanical properties | 10-70 wt% | [3] |
| NR and SBR | morphology and mechanical properties | 50wt% | [332] |
| NR | mechanical properties | 20-30wt% | [333] |
| NR | thermal stability and mechanical properties | 15wt% | [334] |
| NR | thermal and mechanical properties | 5-40wt% | [335] |

SBR=styrene-butadiene rubber; NR= natural rubber

### 5.4 Lignin based carbon fibres

The first studies on carbon fibres production using lignin were carried out in the 1960s. Otanie et al. [336] produced lignin carbon fibres (LCFs) from several types of lignin (alkaline lignin, thiolignin, and lignosulfonate) using different techniques such as: dry spinning, wet spinning and melt spinning. Nippon Kayaku commercialised LCFs with the name "kayacarbon" in 1969. Several studies were carried out using these fibres for example: Tomizuka et al [337] studied the voids and structure of these LCFs. At that time, the vast majority of the studies only considered wet spinning as a production technique for LCFs thus, high molecular weight polymers such as; poly(vinyl alcohol) (PVA), or poly(acrylonitrile) (PAN) were needed to improve the processability of lignin solutions. Utilising this method tensile strength values around 0.8 GPa were reported [337,338]. During the early 1990s, several studies were focused on melt spinning for producing lignin carbon fibre precursors this offers the advantage of not requiring solvents. The main difficulties are that lignin needs to be fusible and a stabilization step is needed prior to carbonisation. During the stabilisation step the thermal behaviour of lignin changes from thermoplastic to thermoset thereby allowing the precursor fibres keep their shape during the carbonisation step. In general, for lignin stabilisation long times are required due to the slow heating rates between 0.1-2 K/mim. Sudo et al. [339] reported the synthesis of phenolated lignin for carbon fibre production. The fibres were previously stabilised at 220-280 ºC and they achieved tensile strength values around 0.45 GPa with a carbon yield of 40 %. Uraki et al. reported the preparation of carbon fibres from organoslv lignin [340]. They acetylated lignin in order to improve its spinnability. In addition, lignin was fractionated in low and high molecular weight fractions in order to study their behaviour during the spinning process. Precursor fibres were carbonised at 1000 ºC previously stabilised at 250 ºC using a heating rate of 0.5 K/min. However, the mechanical properties were very low (tensile strengths of 0.36 GPa) due to the presence of voids in the carbon fibres. At that moment, the main

problems for melt spinning lignin are associated to the thermal behaviour of lignin and its high brittleness. For these reasons, lignin polymer blends have been studied as carbon fibre precursors. The addition of a thermoplastic polymer to lignin improves two important aspects. On the one hand the precursor fibres are less brittle and on the other hand the thermoplastic behaviour of lignin is improved. In 2002 Kadla et al. reported the synthesis of carbon fibres based on lignin/poly(ethylene oxide) (PEO) blends using kraft lignin, without any chemical modification [341]. The PEO content was 5-25 % and they achieved tensile strength values of 400-550 MPa and elastic modulus 30-60 GPa. Later on, Kubo and Kadla published the effect of the synthetic polymer (PP and PET) and lignin blends on fibre properties [342]. The immiscibility between PP and lignin generates a porous structure in the final carbon fibre producing lower mechanical properties (167 MPa tensile strength and 28 GPa modulus) compared to lignin/PET blends (700 MPa tensile strength and 94 GPa modulus) that were completely miscible. Lignin copolymers with PAN were developed by Maradur et al. using radical copolymerization in DMSO [343]. Fibres were produced by wet spinning showing good morphology however, mechanical values of the carbonised samples were not provided by the authors. A thermally fusible softwood lignin, isolated by solvolysis with a mixture of polyethylene glycol 400 (PEG 400) and sulfuric acid, can be easily formed into fibres by melt-spinning at temperatures ranging from 145 to 172 °C without any modification. These lignin fibres could be converted into infusible fibres as a precursor for carbon fibres by conventional oxidative thermal stabilization processing in air or a stream of oxygen [344]. From 2012 to 2014 PEO/lignin blends were dominating the studies on carbon fibres produced by melt spinning [345] but the values of mechanical properties (400-600 MPa tensile strength and 30-40 GPa modulus) were still poor compared to PAN fibres. In 2015 composite fibres from lignin, polyacrylonitrile, and carbon nanotubes (CNT) were successfully fabricated by gel spinning and carbonised [346]. Mechanical properties were studied for those fibres and high values of

tensile strength 1.4 GPa and elastic modulus, 200 GPa were obtained. Biopolymers such as poly(lactic acid) were also used in lignin blends for carbon fibre production [347]. The immiscibility between PLA and lignin generated a heterogeneous morphology along the carbon fibres reducing the mechanical properties compared with pure lignin fibres. Values of tensile strength of around 160 MPa and 11 GPa of modulus were obtained with 20 % PLA content in the precursor fibre. In 2016, Qu et al. reported the study of carbon fibers produced from lignin-derived phenolic oil [348]. Pyrolytic lignin was isolated from pyrolysis oil of red oak. The fibres were processed into carbon fibres through melt-spinning, oxidative stabilization and carbonization at 1000 °C giving tensile strength and modulus values of around 1014 MPa and 122 GPa, respectively. More recently, other polymer blends based on lignin have been developed. Thermoplastic elastomer polyurethane was used to increase the melt spinning processability of organosolv and modified kraft lignin [98], due to the good miscibility between then (see Figure 3). Carbonized fibres showed good values of mechanical properties of tensile strength, 1 GPa and elastic modulus 80 GPa. In addition, those kinds of lignins (organosolv and modified kraft lignin) were evaluated from the point of view of thermal and dielectric behaviour determining that organosov lignin is more suitable than kraft lignin for carbon fibre production [5]. Recently, kraft lignin was fractionated using solvents-based systems involving acetic acid + water in order to isolate the higher molecular weight fractions [349]. The results in terms of mechanical properties were promising achieving tensile strength and modulus of 1.39 GPa and 98 GPa respectively, representing the highest mechanical properties ever obtained for carbon fibers derived from low-cost, chemically unmodified lignin. Although, the mechanical properties of lignin based carbon fibres are being increased, further investigations are required in order to produce carbon fibres from lignin which can adequately replace PAN based fibres. Understanding and promoting crosslinking reactions during the stabilisation and carbonisation

step can play an important role in future investigations for high performance lignin based carbon fibres.

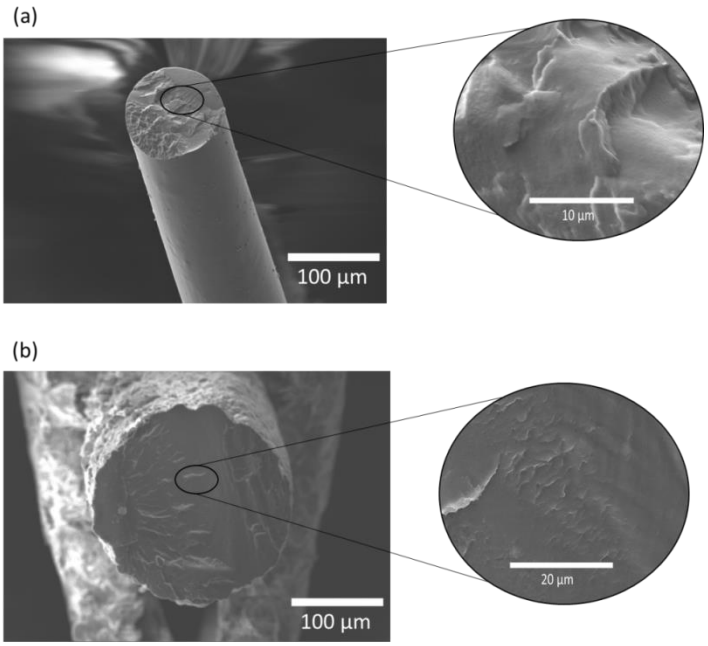


**Figure 3**. SEM images of the cross section of (a) organoslv/TPU and (b) modified-Kraft/TPU preurosr fibres. Reproduced with permission from [98]

## 6 Applications of lignin-based polymer materials

### 6.1 Lignin as source of phenol in thermoset resins

Generally, adhesives for wood materials are based on the combination of formaldehyde with resorcinol or phenol, urea, on epoxy resins and on polyurethanes. Although all these polymers exhibit high tensile strength, they present drawbacks, such as the release of the carcinogen formaldehyde, flammability and the use of supplemental additives, which are usually toxic. Based on its polyphenolic structure and its similarity to phenolic resins, lignin can be added as an ingredient to phenol-formaldehyde resins, displacing phenol (and some formaldehyde) to prepare wood adhesives. Several properties of lignin, such as low glass transition temperatures

[165], low polydispersity [350], and high hydrophobicity make lignin appropriate to be used as adhesive for engineered wood like plywood panels, chip, fiber and wafer board [167]. Although lignin satisfies the requirements of a raw material for the synthesis of bio compatible adhesives, its chemical heterogeneity is a limiting factor. Moreover, lignin is processed using different chemical processes, and each process has its own advantages/disadvantages. The processing methods of the lignin have a significant influence on the adhesive properties of the synthesized phenol-formaldehyde adhesives [351].

There are two groups of lignin-based adhesives: phenol-formaldehyde adhesives when lignin is used as a partial replacement of phenol, and formaldehyde-free adhesives when lignin reacts with chemicals other than formaldehyde to generate bio-adhesives with less toxicity.

Lignin-based phenol-formaldehyde (PF) resins are synthesized by an electrophilic substitution of the phenolic groups located in ortho positions of lignin with formaldehyde. Among different types of lignin, such as lignosulfonates, Kraft lignin, organosolv lignin, enzymatic hydrolysis lignin, and soda lignin, Kraft lignin was evaluated as desirable for the substitution of phenol because of its more free-ring positions, higher molecular weight and thermal decomposition temperature by comparison with other types of lignin [352]. Table 8 presents some examples of different lignin-based phenol-formaldehyde adhesives reported in the literature, the replacement level of phenol in the synthesis of phenol-formaldehyde resin, and the properties investigated by authors.

**Table 8**. Lignin-based phenol-formaldehyde adhesives

| Type of lignin | Level of substitution | Investigated properties | Reference |
|---|---|---|---|
| methylolated lignosulfonate | 30 wt% | water absorption, thickness swelling and flexural strengths | [351] |
| organosolv lignin | 50-70wt% | thermo-mechanical properties | [133] |
| lignosulfonate | up to 50 wt % | shear strength in both wet and dry conditions | [353] |
| methylolated softwood ammonium lignosulfonate | 30% | chemical structure, thermal stability, and rheological behavior | [354] |
| Kraft lignin | 7 wt % and 15 wt % | water resistance | [355] |
| Kraft lignin | 50 wt % | modulus of elasticity, modulus of rupture, internal bonding strength, water absorption, and swelling thickness | [356] |
| Kraft lignin | 30 wt % | shear strength | [357] |
| Kraft lignin | 50wt% | mechanical and physical properties | [358] |
| hydroxymethylated lignin | 10–40 wt% | water resistance | [359] |
| enzymatic hydrolysis lignin | 10–60 wt %, | adhesive strength | [360] |
| methylolated organosolv lignin | up to 50 wt% | tensile strength | [361] |
| organosolv lignin | 25 to 75 wt% | thermal stability | [362] |
| lignocellulosic ethanol residue | 10–70 wt% | thermal stability | [363] |
| enzymatic hydrolysis lignin | up to 55 wt% | physical, chemical, thermal, and mechanical properties | [364] |
| hydroxymethylated lignin | 40 wt% | bonding strength | [365] |
| methylolated bio-oil-phenol formaldehyde | up to 75 wt% | physical, chemical, thermal, and mechanical properties | [366] |
| bagasse lignin | 30wt% | physical properties | [367] |
| phenolated lignin | 50 wt% | physical, chemical, thermal, and mechanical properties | [368] |
| Kraft lignin | 20 wt% | mechanical properties, stiffness, internal bond | [369] |
| enzymatic hydrolysis lignin | 10-20 wt% | bonding strengths | [370] |

### 6.2 Formaldehyde-free lignin-based adhesives

Lignin has lower reactivity toward formaldehyde compared to phenol and the incorporation of unmodified lignin to phenolic resin formulations is restricted to a low replacement level and shows a reduction in adhesion strength with a longer pressing time [371]. Most studies on synthesis of lignin-based adhesives without formaldehyde report the use of glyoxal [372-376] a non-volatile non-toxic dialdehyde but less reactive than formaldehyde, furfural [377] and, more recently, glutaraldehyde [378]. Calcium lignosulphonate reacted with glyoxal under alkaline condition, and the resulting lignin was mixed with polymeric diphenylmethane diisocyanate (pMDI) and applied as wood adhesives for particleboard applications [375]. The formulation containing 4,4´-diphenyl methane diisocynate (pMDI), different ratios of methyolated lignin and glyoxal as substitute of formaldehyde in particleboard showed excellent internal bonding strengths in dry and boiled conditions in a ratio of 60/40 wt% of glyoxalated lignin/pMDI adhesive [372]. Glyoxalated lignin with a low molecular weight in the formulated pMDI shows a better internal bonding strength.

Introduction of triacetin into the lignin-based adhesives enhanced the curing process of the methylolated lignin with pMDI and improved the modulus of elasticity value [378]. Glyoxalated lignin mixed equally with tannin, followed by crosslinking with hexamine (5 wt % of tannin) was reported as a bio-based adhesive without incorporating any synthetic resin [373,379]. Another formaldehyde-free resins showed good thermal stability and char yield [380]. A formaldehyde-free wood adhesive using Kraft lignin and polyethylenimine (PEI) was designed for the manufacture of plywood. The sample containing lignin/PEI in weight ratio of 2:1 showed the highest shear strengths (dry shear strength, water-soaking- and drying strength, boiling water test/dry strength, and boiling water test/wet strength) and the greatest water resistance [381,382]. The physico-mechanical properties of a modified ammonium lignosulfonate (AL)/PEI mixture as a green binder in preparation of medium density fiberboard

(MDF) were evaluated [383]. The optimum performance was obtained at 20 wt % binder with AL /PEI weight ratio of 7:1 after curing at 170 °C for 7 min. The relative crystallinity of the composites was significantly improved. A combination of polyfurfuryl alcohol (PFA) and lignin, where furfural and lignin replaced formaldehyde and phenol in polyphenol (PF) resins, respectively, were prepared in lignin contents of 20 and 30 wt % [384].

The presence of lignin led to the formation of a slightly stiffer matrix with better impact strengths. Similar lignin-furfural based adhesives show a better performance because the lower molecular weight of lignin has better mobility and exhibited better mechanical properties. The influence of furfural content, pH, curing temperature and pressure on the mechanical properties were studied [377]. Enzymatic hydrolysis lignin (EHL) performed in oxygen plasma improved the physical and mechanical properties of EHL. The modulus of elasticity, modulus of rupture, and internal bonding strength increased while thickness swelling decreased with increasing the time and power of the plasma processing [385].In a recent study phenol portion from phenol formaldehyde resin was replaced by an agricultural-based lignin, which was produced as a byproduct of a cellulosic bioethanol process through dilute-acid pretreatment and enzymatic hydrolysis from corn stover. The PF resol resin was formulated using isolated lignin under alkaline condition [386].

### 6.3 Lignin-epoxy resins

Noteworthy, there have been several reports in the literature that presents the interest in preparing lignin-epoxy resins. For these applications the waste lignin derived from the common pulp and paper processes (Kraft, soda, etc.) must be purified (precipitation, deionisation, etc.) or one can use lignin from the less condensing pulping processes such as Alcell, non-wood fibres pulping. Phenolated Kraft lignins with different purity degrees were prepared and tested as adhesives for plywood. When the phenolation of Kraft lignin was acid catalyzed the strength and water resistance of the final resin were higher. The experimental tests evidenced that lignin

purity did not influence the adhesive properties of the resulting resins [387-389]. Some scientific papers show that significant lignin loads (<50 wt%) could be incorporated into the epoxy resin and they exhibited good electrical (dielectric constant, loss in dielectric tangent angle and dielectric rigidity, volume and surface resistivity,) and mechanical properties, as well as high impact toughness (Charpy impact strength) as compared with the lignin free phenol epoxy resins [390-392]. Later on, lignin was incorporated into the resin for fabrication of printed circuit boards [393]. Some other reports show that epoxy modified lignin-based resins can be prepared in significant quantities by purification techniques involving reaction of lignin with epichlorohydrin and subsequent recycling of excess of epichlorohydrin and filtration to purify the resulting resin [388,394].

### 6.4 Lignin based nano carbon fibres for energy storage devices

Currently, there are several kinds of devices able to store energy such as: fuel cells, batteries, combustion engines, supercapacitors and capacitors [395,396]. Basically, there are two parameters characteristic for all devices employed in energy storage, one is the energy density and the other one is the power density. The energy density gives information about the amount of energy that the device can accumulate per unit mass, the power density is related with the power output that the device is able to supply per unit mass. Batteries show high energy density however low power density; in contrast capacitors exhibit a high power density and low energy density. Consequently, batteries store energy well, however the energy output is low. On the other hand capacitors are able to fast supply energy, however, they cannot store energy well. In the region with intermediate properties are the supercapacitors. During the last decade, carbon nanofibers (CNFs) produced by electrospinning have been studied as electrodes for both kind of devices, supercapacitors and batteries. Although, the vast majority of studies published until

now, use PAN as precursor material [397], below we describe the few papers that use lignin based precursors.

Lai et al published the synthesis of electrospun CNFs made from lignin/PVA solutions [398]. The gravimetric capacitance of CNFs produced from lignin/PVA(70/30) exhibited 64 $F.g^{-1}$ at 400 $mA.g^{-1}$ and 50 $F.g^{-1}$ at 2000 $mA.g^{-1}$. The CNFs electrodes also exhibited excellent cycling durability/stability, and the gravimetric capacitance only was reduced by around 10% after 6000 cycles of charge/discharge. In 2015, You et al. [399] reported the preparation of Lignin-based activated carbon fibers by electrospinning of hardwood acetic acid lignin. These CNTs showed good capacitance, 133.3 F $g^{-1}$ at a current charge of 1 A $g^{-1}$. High energy and power density for this device (42 Wh $kg^{-1}$ and 91 kW $kg^{-1}$, respectively) were also achieved. Electrodes produced from soda lignin and PEO CNFs show good potential for supercapacitors as was reported by You et al. [400]. Lignin/PEO CNFs electrodes with an organic electrolyte exhibited an impedance of 1.6 Ω and a specific capacitance of 92.6 F $g^{-1}$ at a scan rate of 1 A $g^{-1}$. In addition, hybrids materials based on PAN/lignin/$NiCo_2O_4$ were studied by Lei et al in 2017 [401]. They produced PAN/lignin based carbon nanofibers with different contents of lignin. Afterwards, the $NiCo_2O_4$ oxides were deposited on the surface of CNFs by hydrothermal reaction. They developed flexible PAN/lignin/$NiCo_2O_4$ CNFs electrodes giving a high specific capacitance of 1757 F $g^{-1}$ at 2 mA $cm^{-2}$ and excellent cycle resistance with 138% of capacitance retention after 5000 cycles at 7 mA $cm^{-2}$.

There are only a few examples of electrodes made from lignin based solutions in the last decade. Nitrogen-doped free standing fused carbon fibrous mat, fabricated from organosolv lignin/ PEO (90:10) blend via electrospinning followed by carbonization and thermal annealing in the presence of urea, was prepared by Wang et al. [402]. The fused carbon fibres without nitrogen doping exhibited high specific capacity up to 445 mA h $g^{-1}$ at a current density of 30 mA $g^{-1}$ (comparable to PAN derived carbon nanofibers) and good cyclic stability at different current

rates. After thermal annealing in the presence of urea, the charge capacity was further improved to as high as 576 mA h $g^{-1}$ and still maintained a good capacity of about 200 mAh $g^{-1}$ even at a high current rate of 2000 mA $g^{-1}$. In 2014 Jin et al. reported CNFs electrodes for sodium ion batteries made from PAN/lignin solutions [403]. With a mass ratio PAN/lignin of 5/5 which exhibit a high reversible capacity of 292.6 mA h $g^{-1}$ with an initial efficiency of 70.5% at a constant current density of 0.02 A $g^{-1}$. Research on lignin based batteries is currently at an early stage. There are difficulties associated with electrode preparation as some lignins are impossible to stabilise and therefore convert to carbon nanofibres and due to the occurrence of irregular morphologies as a result of electrospinning low viscosity lignin solutions.

### 6.5 Lignin-based hydrogels

Hydrogels are defined as physically or chemically cross-linked three-dimensional hydrophilic networks that swell in water or aqueous solutions. Hydrogels present interesting properties such as highly water absorption and retention, good biocompatibility, tissue-mimicking ability, and controlled diffusion [404], making them suitable for a large number of applications such as tissue engineering, absorption, drug delivery and biosensors [405]. Hydrogels can be synthesized using several methods including free radical polymerization, irradiation, as well as chemical and physical cross-linking of polymers. Lignin has become the focus of many studies in the field of hydrogel development due to its inherent properties such as biocompatibility, biodegradability, low toxicity, and importantly its susceptibility to enzymatic degradation [405]. Early works have shown that the preparation of lignin hydrogels by graft copolymerization between acrylamide (AM) and poly(vinyl alcohol) (PVA) with alkaline or kraft lignin (AM-PVA-g-lignin) and then by mixing with acrylamide monomer was possible [406]. Compared with Kraft lignin hydrogel, the alkaline lignin hydrogel showed very high swelling ratios and slower water uptake and deswelling rates which can be attributed to its

network structure [406]. Xanthan-lignin networks were reported by Raschip et al. [407] as being obtained by crosslinking xanthan and lignin in the presence of epichlorohydrin. This study showed that the structure of lignin strongly influenced the swelling process. Poly(ethylene) glycol diglycidyl ether (PEGDGE) has also been utilised as a crosslinker for several technical lignins (see Figure 4) producing highly swollen gels, which exhibited mechanical stability [408]. The authors suggested that that these gels could potentially be used for minimizing drought stress and enhancing irrigation efficiency, especially in sandy soils with low water retention in arid regions. Polyurethane/lignin hydrogels have been obtained by reacting acetic acid with lignin and isocyanate group-terminated polyurethane ionomers [409]. Those hydrogels possessed pH-sensitivity and showed potential as coating materials for slow-release fertilizers [409].

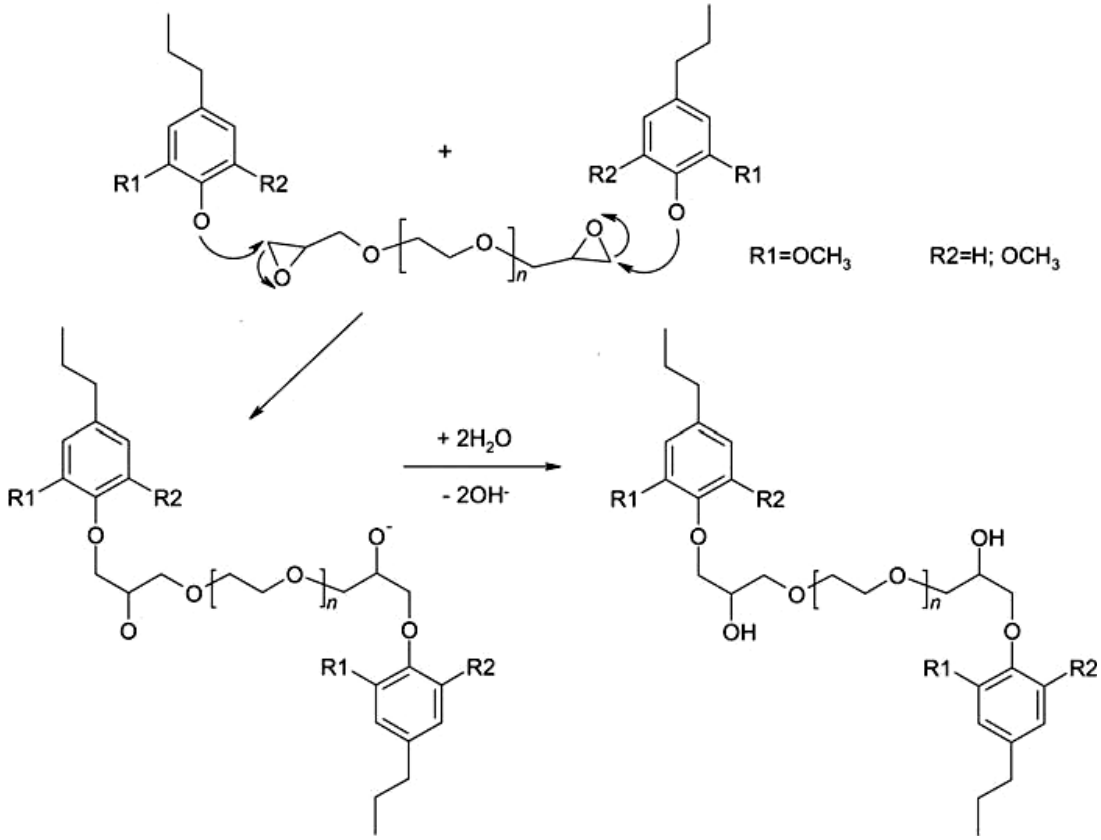


Figure 4. Reaction scheme of PEGDGE-mediated cross-linking of lignin substructures under alkaline conditions. Reproduced with permission from [408]

Bentonite/sodium lignosulfonate graft-polymerized with acrylamide and maleic anhydride (BLPAMA) have produced hydrogels for lead removal reaching a $Pb^{2+}$ adsorption capacity of 1.045 mmol/g at pH=5.0 [410]. Similar investigations were carried out by Xiaodong Zhang, et al. using lignin/clay hydrogels for dye (methylene blue) removal [411]. These hydrogels were prepared by grafting acrylamide and *N*-isopropyl acrylamide onto lignin, along with the incorporation of montmorillonite assisted by ultrasonication (lignin-g-p(AM-co-NIPAM)/MMT) as it was shown in Figure 5. The adsorption data fitted well the Langmuir and Freundlich models, with an optimum adsorption value of 9646.92 mg/g. Other hydrogels were prepared starting from lignin and poly(ethylene glycol) methyl ether methacrylate (PEGMA)/cyclodextrin (α-CD) by atom transfer radical polymerization [412]. These hydrogels showed mechanically responsiveness, good rheological properties and excellent self-healing ability. Given their lignin biodegradable core, the hyperbranched supramolecular hydrogels are expected to be potentially biodegradable. Drug delivery is one of the applications for lignin based hydrogels as reported by Xiaohong Wang, et al [413]. Sodium lignosulphonate-grafted poly(acrylic acid-co-poly(vinyl pyrrolidone)) hydrogel (SLS-g-P(AA-co-PVP) was prepared by ultrasound-assisted synthesis. Amoxicillin was used as model drug to study the release properties. It was found that the release behaviour can be controlled by adjusting the pH value of the medium. In simulated gastric fluids (SGF) (pH around 1.2), the cumulative release rate was up to 51.5% in 24 h and about 32% for 2 h. But for the simulated intestinal fluids (SIF) (pH around 7.4), the cumulative release rate reached 84.5% in 24 h and 63.3% after digestion and absorption for 5 h [413].

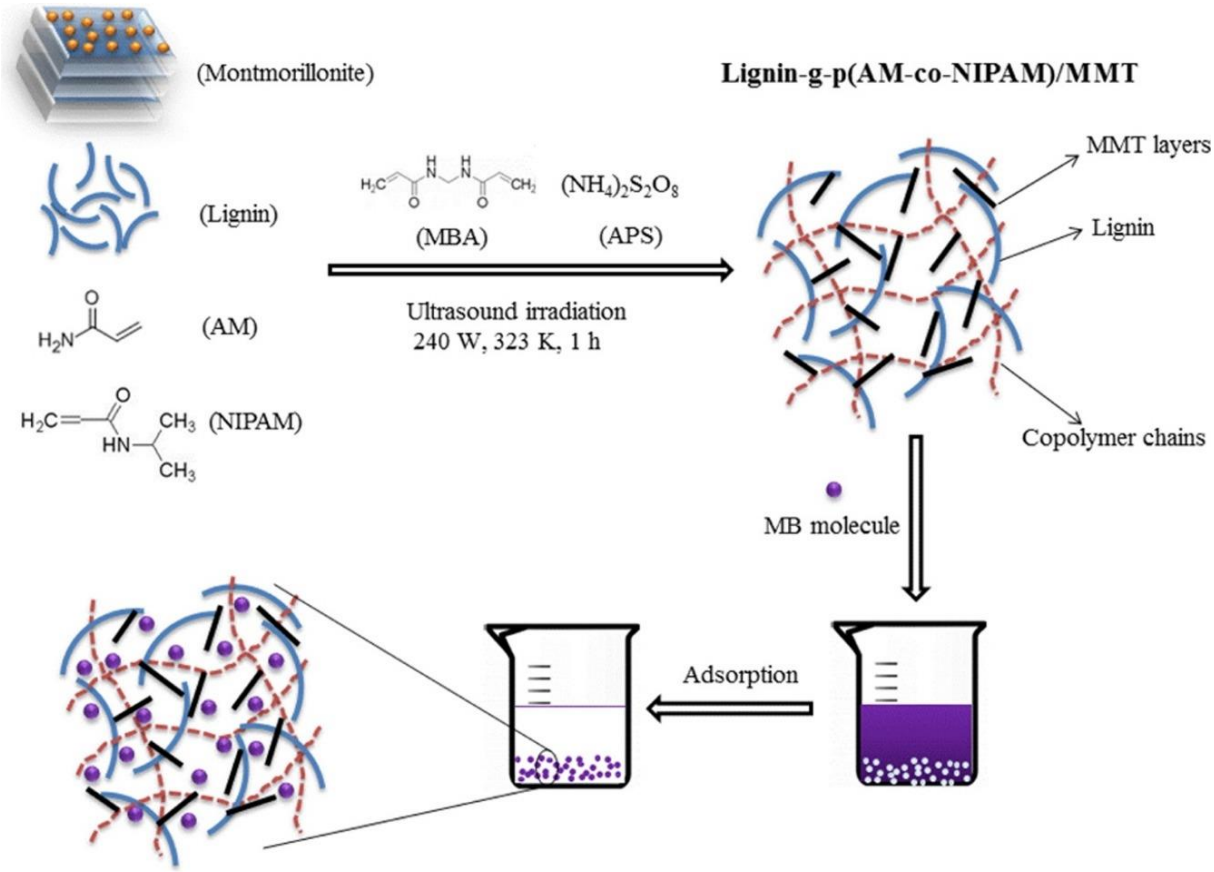


Figure 5. Schematic process of the preparation and adoption process of lignin-g-p(AM-co-NIPAM)/MMT. Reproduced with permission from [411]

Hydrogels based on soluble glycinated Kraft lignin (WS/KL) and hyaluronan (NaHy) were prepared [414]. The lignin was modified by a Mannich reaction in order to improve the water solubility of lignin. It was found that the creep resistance and creep recovery of NaHy hydrogels were improved by the incorporation of WS/KL up to 3% (w/w). However, the swelling capacity of hydrogels was low, but the cytotoxicity tests demonstrated that the final hyaluronan/lignin hydrogels were non-toxic materials.

The combination of cellulose and lignin has been also studied in order to develop hydrogels [415,416]. Reinforced PVA hydrogels containing lignin and cellulose nanofibrils were obtained and it was shown that the mechanical and rheological properties of the reinforced PVA

hydrogels can be tuned by varying lignin and cellulose content [415]. In addition, lignin and cellulose can be combined in supercapacitors as it was reported by Wenbin Zhong, et al. [416]. They produced electrodes using SWCNTs dispersed in lignosulfonate solutions submitted to an autoclave hydrothermal treatment at 180°C for 12 h. Cellulose hydrogels were used as electrolyte mixed with NaOH solutions. The supercapacitors showed excellent electrochemical stability (1000 bending cycles) and specific capacitance values of 292 F/g.

There is little doubt about the potential valorisation of lignin through its use in hydrogel formulations due to the large number of applications in energy storage, biomedicals and pharmaceutics, adsorbents and electrochemical sensors. Looking to the future it is likely that the deployment of lignin based hydrogels will be in conjunction with newly developed processing techniques such as advanced printing technologies.

### 6.6 Other Lignin types and applications

Lignin has been identified as a potential renewable source of biodegradable and safer antioxidants and stabilisers. Substantial work has been reported to date on the identification of material charactersitics that are critical to tailor the antioxidant and stabilising effects of differing lignins [35,51,146]. It is clear that the performance of lignin strongly depends on its origin, extraction method and subsequent modification as described previously [417]. It is generally agreed that lignin acts as an antioxidant through scavenging of free radicals. For example, the importance of non-etherified phenolic hydroxyl groups (acting as scavengers of peroxyl radicals) has been demonstrated [58,418]. While it has been demonstrated that structural variations such as higher molecular weights and polydispersity were detrimental on antioxidant activity [418,419]. Radical scavenging ability also plays an important role on thermal stabilisation of lignin, therefore increased phenolic contents offer superior thermal

stability in blends with other polymers [52] highlighting that thermo-oxidative stabilisation activity is strongly related to antioxidant activity for lignins.

Poly-(caffeyl alcohol) (PCFA) homopolymer called C-lignin was recently discovered in the seed coats of Vanilla orchid (*Vanilla planifolia*) [420] and various cacti species [421]. Structural analysis reveals that the polymer is a benzodioxane chain derived entirely from caffeyl alcohol monomers (G units lacking the methyl group on the 3-oxygen) linked head to tail via radical coupling reaction. It is postulated that the homogeneity of the polymer could potentially improve biomass utilisation as depolymerisation of lignin to a single product can be controlled, as schmatically shown in figure 6 [422-424]. C-lignin extracted from Vanilla seeds has been successfully electrospun into fibres without any chemical pretreatment or addition of other polymers [425]. Following carbonisation at 900°C, carbon fibres from C-lignin had a diameter of about 10μm, comparable axial moduli and superior transverse moduli compared to Kraft and commercial CF. However despite this potential in engineering applications, its commercial value remains unclear as it is not available in bulk quantities from traditional biomass sources.

Another new type of lignin, called 5H lignin, has been identified via NMR analysis of *Escobaria dasyacantha* seeds [421]. This type of lignin is derived from polymerisation of 5-hydroxyconiferyl alcohol (S unit lacking methyl group at position 5 of the aromatic ring).

Thermoelectricity could be another potential application for lignin allowing the production of energy from temperature gradients. Thermoelectric effects have been observed in carbon nanofibres derived from ligin, with authors able to obtain p-type to n-type semiconducting behaviour with a thermoelectric power factor of 9.27 $\mu W\ cm^{-1}\ K^{-2}$ [426]

In summary, Lignin structures and yields in transgenic plants have been the focus of extensive research [6]. While these attempts to control the structure or yield of lignin have also provided important information about its biosynthetic pathways.

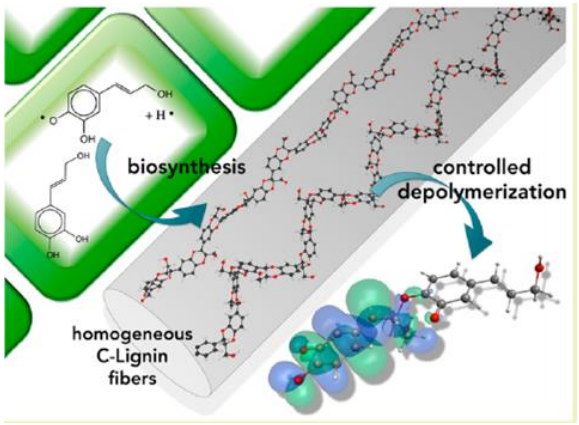

Figure 6. Schematic representation of C-lignin and its potential for controlled depolymerisation.

## 7 Concluding remarks and future developments

Lignin is the most important aromatic polymer derived from renewable resources, it displays both a unique and complex chemical structure, is abundant in nature and does not compete with the food production chain. Lignin remains a subject of strong interest in industry and academia, as vouched by the impressive amount of data accumulated lately in the literature. Despite the knowledge and technical progress in terms of its valorization, much as yet to be achieved. Progress has been made on its role as a resource for the production of renewable fuels and chemicals mainly associated with recent advances reported in bioengineering, biorefining and catalysis. However, research on lignin as a precursor for carbon fibre at both micron and nanoscale is in its infancy. The future potential of lignin in medicine and healthcare, pharmaceutics and cosmetics, food packaging and energy is yet to be established and is sure to the subject of investigations in the coming years.

Future research directions are likely to be aimed at developing nanostructured materials for advanced applications (energy storage, thermoelectric devices, bio-sensors, controlled drug delivery, gene therapy, theranostic systems). Investigations are required to establish the complex interactions of these newly designed materials with living tissues, to determine targeting cues and to provide solution based on controlled release mechanisms,

chemical/enzymatic degradation activity under physiological conditions need to be taliored, while elimination procedures to avoid tissue accumulation and side effects must be realised.. Once these principles are established it is likely that lignin will play a role in the development of 3D printing and bioprinting technologies [395 427].

Ultimately, the valorization of lignin will be strongly influenced by its chemical and functional versatility, which will demand specific approaches in terms of processing and chemical modifcation. The next steps in this direction will involve the understanding of structure/property/function relationships in these materials while offering the possibility of tuning the macroscopic properties of the materials through the control of the structure,morphology and chemistry at nano scale.

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